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6. AUTHOR(S)
M. GREGORY FOREST

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL
DEPARTMENT OF MATHEMATICS
CB# 3250, PHILLIP HALL
CHAPEL HILL, NC 27599-3250

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13. ABSTRACT *(Maximum 200 words)*

Our early work centered upon microstructure coupling with strong flows, which include fiber spinning arid general extensional flows. These remain the most successful flow-processing regimes for high-performance materials because hydrodynamics dominates the microscopic physics. In essence, most commercial high-performance polymers are processed through fiber spinning, following Nature and spider silk, which is still pound-for-pound the toughest liquid crystalline polymer. Our work has contributed toward the derivation of models, their analysis and computation, leading to quantitative models for steady, robust, and controllable microstructure alignment in extension-dominated liquid crystalline polymer flow processes [1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 93. The current major efforts in materials design are toward fabricating 2 and 3 dimensional products, from thin films to solid structures. The highly successful fiber processes are not scalable: one has to weave volumes of fibers to make higher dimensional products, and then one only has homogenized averages of anisotropic fiber properties, where the averages must arise from mixing filaments. So one has to leave the 1 dimensional world of fibers and study either film flows or general mold-filling type flows. Such processes arc dominated by shear components, which are weak flows marked by linear particle trajectories as opposed to exponential streamlines of extension-dominated flows.

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HIGH-PERFORMANCE MACROMOLECULAR MATERIALS

AFOSR Contract F49620-01-1-0008

M. Gregory Forest
Department of Mathematics
University of North Carolina at Chapel Hill

Final Progress Report

Objectives & Overview

The primary goals of this research proposal consist of the development of mathematical theory and computational tools for the design and processing of high–performance, macromolecular materials. These materials are comprised of easily synthesized, anisotropic molecular elements, ranging from rod-like to platelet geometries. These materials are processed in the liquid phase, where they undergo disorder-order transitions above a critical concentration. When driven by flow processing, these ordered phases are modified and disrupted, generating structures at the micron scale that remain uncharacterized. In turn, these molecular structure properties are responsible for the targeted performance enhancement features (electrical or thermal conductivity, strength, resistivity to penetration by gases or chemical species or wavelengths of light). The design and control pipeline can therefore be divided into two fundamental theory and computation problems:

- Molecular and process controls determine the micron-scale structures generated in films and molds. The mathematical models, analytical methods, and simulation tools for these structure properties generated in laminar confined flows are the central components of our research over the past three years.

- Once the micron-scale molecular morphology is characterized, either as a numerical database or through analytical scaling properties, the next challenge to mathematics and computation is the determination of material performance properties from the combination of molecular properties, the solvent or matrix properties in nano-composites, and the geometry of the material (film thickness, mold shape). This second phase of the pipeline has just begun to be accessible based on the results of our research.

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Status of Effort

Our early work centered upon *microstructure coupling with strong flows*, which include fiber spinning and general extensional flows. These remain the most successful flow-processing regimes for high-performance materials because hydrodynamics dominates the microscopic physics. In essence, most commercial high-performance polymers are processed through fiber spinning, following Nature and spider silk, which is still pound-for-pound the toughest liquid crystalline polymer. Our work has contributed toward the derivation of models, their analysis and computation, leading to quantitative models for steady, robust, and controllable microstructure alignment in extension-dominated liquid crystalline polymer flow processes [1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 9].

The current major efforts in materials design are toward fabricating 2 and 3 dimensional products, from thin films to solid structures. The highly successful *fiber processes are not scalable*: one has to weave volumes of fibers to make higher dimensional products, and then one only has homogenized averages of anisotropic fiber properties, where the averages must arise from mixing filaments. So one has to leave the 1 dimensional world of fibers and study either film flows or general mold-filling type flows. Such processes are dominated by shear components, which are *weak flows* marked by linear particle trajectories as opposed to exponential streamlines of extension-dominated flows.

All experiments and models show that the macromolecular response to weak flow is extremely complex–indeed even anomalous, with outcomes sensitive to flow rate, molecular concentration, and details of the molecular architecture. These issues form the core of our research program.

We collaborate with several experimental groups, including Dr. Richard Vaia, Materials Directorate, Wright-Patterson AFB, Dr. Pat Mather, U. Connecticut and formerly at WPAFB, and K. Koelling, Ohio State U. and a former colleague of Forest. All of our results are presented at professional scientific meetings and in the premier scientific and engineering journals.

One is confronted with several fundamental obstructions to the molecular-to-macroscopic design goal of 2 and 3 dimensional macromolecular materials. These limitations all have mathematically challenging underpinnings. Without fundamental advances, the technology will remain empirical and far from optimized.

First, the theory for concentrated solutions of complex molecules, either

in highly concentrated phases or in mixtures with solvents, remains an open active area. That is, *the equations are not definitively known.* For idealized fluid systems consisting of a solvent with molecules assumed to be rigid axisymmetric ellipsoids, we [13, 15] have a kinetic theory that extends the seminal work of Doi, Marrucci and Greco. Even for imposed homogeneous flows, this theory yields an infinite-dimensional, nonlocal Smoluchowski equation for bulk steady and dynamical responses. The literature is replete with attempts to derive moment-closure approximations of kinetic theory, which project the probability distribution function (pdf) onto a mesoscopic tensor system for the second-moment of the pdf. Our results over the past year [18, 14, 21, 17, 20, 23] address the *upscaling and downscaling (bridging molecular and micron scales) between microscopic kinetic theory and moment-averaged models.*

Second, when complex fluids are processed, complex orientational patterns emerge on lengthscales that were not consciously put into the problem, unrelated to the experimental apparatus, the flow, or the molecular potentials. These mesoscopic (micron-scale) structures emerge from nonequilibrium interactions between the flow, microstructure, geometric confinement, and boundary conditions. These mesoscopic structures are not yet understood, and are only now being modeled with current theory and simulations. There were no exact models for these mesoscopic structures, so we derived *families of exact equilibrium patterns* that are supported purely by material properties [7, 8]. These exact solutions are mathematical models which serve as candidates for pattern selection mechanisms in flow. We have also derived special singular solutions of the flow-nematic equations to model what are known as core defects in extensional flows [4].

Our major efforts have recently gone into understanding *coupled flow & microstructure phenomena in shear-dominated flows.* We first derived a model system for the onset and evolution of structure, both in the flow field and in the molecular orientation field, in a typical shear cell. Shear devices are the primary tool by which flow properties of complex fluids are characterized and imaged. Our shear-cell simulations were first benchmarked against weak-shear asymptotics where we can predict scaling properties of structure in the flow and microstructure. These predictions turn out to extend to larger, realistic shear rates. Our more general numerical studies reveal a strong correlation between the bulk orientation response in weak shear flow and the structures which emerge. These bulk homogeneous responses dominate the

early onset of structure development near the mid-plane of the shear cell, with a mechanism we pose through which transient molecular bulk motion transforms into spatial structures. These results comprise two preprints [22, 23].

Armed with evidence that the monodomain response to shear is the precursor to structure formation, we embarked over the past two years on a fundamental understanding of which monodomain states emerge from a quiescent nematic liquid at the onset of shear. The relevant preprints and reprints on this topic are [18, 14, 21, 17, 16, 15, 20, 23, 24]. This work is the foundation for all structure evolution studies now underway.

Personnel Supported

The PI has been supported through summer salary and travel. Postdoc Ruhai Zhou is partially supported. Hong Zhou, UC-Santa Cruz, has been supported as a research consultant.

Transitions

- The PI continues to communicate with scientists at WrightPatterson AFB, Materials Directorate, Dayton, OH. These interactions have led to the current focus on shear-dominated flows, the role of confined geometry, and effects of molecular geometry.

Interactions

Invited lectures at meetings, conferences, and colloquia have resulted from this supported research. Over 12 months:

- 2001, "Mesostructure evolution in tumbling nematic LCPs between shearing plates", 3rd Pacific Rim Rheology Conference, Vancouver, BC, July 9
- 2001, "Shear-induced monodomains of nematic polymers: finite aspect ratio effects", 3rd Pacific Rim Rheology Conference, Vancouver, BC, July 9
- 2001, "Dynamic precursors to structure formation in sheared macromolecular fluids", A.F.O.S.R. Contractor and Grantee Annual Meeting, Stanford, CA, July 24
- 2001, "Dynamics of shear-induced monodomains for finite-aspect-ratio macromolecules", Society of Rheology Meeting, Bethesda, MD, October 21
- 2001, "Dynamic precursors to structure formation in sheared macromolecular fluids", AIChE Annual Meeting, Reno, Nevada, November 4-9
- 2001, "Mathematical aspects of simple flows containing simple molecules", Applied Mathematics Seminar, UNC-CH, November 16

- 2001, "Monodomain presursors and mesostructure evolution in linear and nearly linear flows of rigid, ellipsoidal macromolecules", Materials Research Society Fall Meeting, Boston, MA, November 28

- 2002, "The dynamics of nematic liquids in shear and related linear flows", Utah State Workshop on Mathematics in Industry, Logan, UT, March 1-2

- 2002, "The dynamics of nematic liquids: molecular theory and averaged descriptions", University of New Mexico Symposium of the Center for Advanced Studies, Albuquerque, NM, April 18-19

- 2002, "The orientational degeneracy of nematic liquids and its role in the dynamical response to shear flow", Fourth International Conference on Dynamical Systems and Differential Equations, Wilmington, NC, May 24-27

- 2002, "The dynamics of nematic liquids: molecular theory and averaged descriptions", Joint meeting of Italy and U.S. Mathematics Societies, Symposium on Mathematical Problems in Soft Matter Modeling, Pisa, Italy, June 12-16

- 2002, "Free energy characterizations of mechanical incompressibility in thermal viscous flow", Fourteenth U.S. National Congress of Theoretical and Applied Mechanics, Symposium for Dan Joseph, Blacksburg, VA, June 23-28

- 2002, "Dynamic Precursors and Structure Formation in Flowing Nematic Polymers", SIAM Fiftieth Anniversary Meeting, Symposium on Materials Science, Philadelphia, PA, July 10

- 2002, "Microscopic and mesoscopic predictions of nematic polymers in shear-dominated flows", Marrucci Symposium, National Meeting of the Society of Rheology, Minneapolis, MN, Oct. 15

- 2002, "Passing between molecular and mesoscopic descriptions of high-performance macromolecular materials", International Mechanical Engineering Congress and Exposition, New Orleans, LA, Nov. 19

- 2002, "Laminar flows of nematic polymers: molecular theory and averaged descriptions", Northwestern University, Applied Mathematics Colloquium, Evanston, IL, Dec. 5
- 2003, "Laminar flows of nematic polymers: issues critical to high-performance materials", University of Colorado-Boulder, Applied Mathematics Colloquium, Boulder, CO, Jan. 18
- 2003, "Mathematics of high-performance materials", AMS Special Session on the Mathematics of Materials, Rob Lipton, Organizer, Baton Rouge, LA, March 14
- 2003, "Laminar flows of nematic polymers: passing between kinetic and mesoscopic scale models", Workshop on Multiscale Theory and Computation in Nano Materials, Wright-Patterson AFB, Dayton, OH, March 29
- 2003, "What's math got to do with nano-materials?", UNC-Chapel Hill Mathematics Graduate Visions Seminar, April 14
- 2003, "Laminar flows of nematic polymers: high-performance materials in the making", Carnegie Mellon University, Mathematics Department, Pittsburgh, PA, May 1
- 2003, "The dynamics of nematic polymers in laminar flows: a zoo of bifurcations associated with bulk molecular phase transitions", SIAM Dynamical Systems Annual Meeting, Snowbird, UT, May 28
- 2003, "Modeling of Nematic Polymer and Nano-Composite Flow Processing", SIAM Conference on Mathematics for Industry: Challenges and Frontiers, Toronto, Canada, June 23

Honors/Awards None.

Non-research scholarly articles

- "Mathematical challenges in nanoscience and nanotechnology", an essay for the September, 2000, Workshop on "Societal Implications of Nanoscience and Nanotechnology", U.S. Interagency Working Group

on Nanoscience and Nanotechnology, Washington, DC, Kluwer Academic Publishers (2001).

- "Nano-Materials: Can we do the Math?", solicited essay by the American Association for the Advancement of Science, for posting on the EurekAlert! website for international journalists (2002).

Publications and Submitted Articles

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[1] An isothermal model for high-speed spinning of liquid crystalline polymer fibers: Coupling of flow, orientation, and crystallization, (with T. Ueda), Journal of Non-Newtonian Fluid Mechanics **84**, 109-121 (1999).

[2] Near-equilibrium dynamics of Doi models for liquid crystal polymer flows: catastrophic and regularized behavior, (with Q. Wang), Journal of Non-Newtonian Fluid Mechanics **83**, 131-150, (1999).

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[9] A model for a spreading and melting droplet on a heated substrate, (with D. M. Anderson and R. Superfine), SIAM Journal on Applied Mathematics **61**(5), 1502-1525, (2001).

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[12] Transient behavior of thermal optical glass fiber drawing processes, (with H. Zhou), European J. Appl. Math. **12**, 479-496 (2001).

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[14] Symmetries of the Doi kinetic theory for nematic polymers of arbitrary aspect ratio: at rest and in linear flows, (with Q. Wang and R. Zhou), Physical Review E **66**, 031712 (2002).

[15] A hydrodynamic theory for solutions of nonhomogeneous nematic liquid crystalline polymers with density variations, (with Q. Wang and R. Zhou), refereed proceedings of ASME International Mechanical Engineering Congress, N.O., La., IMECE2002-32189 (2002).

[16] Explicit flow-aligned orientational distribution functions for dilute nematic polymers in weak shear, (with Q. Wang and R. Zhou), refereed proceedings of ASME International Mechanical Engineering Congress, N.O., La., IMECE2002-32185 (2002).

[17] Full-tensor alignment criteria for sheared nematic polymers (with R. Zhou, Q. Wang), J. Rheology **47**(1), 105-128 (2003).

[18] Monodomain response of finite-aspect-ratio macromolecules in shear and related linear flows, (with Q. Wang), Rheologica Acta **42**, 20-46 (2003).

[19] Thermal expansion models of viscous fluids based on limits of free energy, (with S. Bechtel, F. Rooney, and Q. Wang), UNC-CH Program in Applied Mathematics Preprint, Physics of Fluids, to appear.

[20] Monodomain response of arbitrary aspect ratio nematic polymers in general linear planar flows, (with Q. Wang, R. Zhou, and E. Choate), UNC-CH Program in Applied Mathematics Preprint, submitted to JNNFM (April, 2003).

[21] The weak shear kinetic phase diagram for nematic polymers, (with Q. Wang and R. Zhou), UNC-CH Program in Applied Mathematics Preprint, Rheologica Acta, under revision (2003).

[22] Structure evolution in tumbling and kayaking nematic liquid crystalline polymers between shearing plates, (with Q. Wang and H. Zhou), UNC-CH Program in Applied Mathematics Preprint, submitted to J. Non-Newtonian Fluid Mech. (April, 2003).

[23] Structure scaling properties of confined nematic polymers in plane Couette cells: the weak flow limit, (with Q. Wang, H. Zhou, and R. Zhou), UNC-CH Program in Applied Mathematics Preprint, submitted to J. Rheology (April, 2003).

[24] Scaling behavior of kinetic orientational distributions for dilute nematic polymers in weak shear, (with Q. Wang, R. Zhou), JNNFM, submitted January, 2003.